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A STUDY OF THE VAPOR PRESSURE OF AQUEOUS SOLUTIONS OF POTASSIUM CHLORIDE AT 20°C

DISSERTATION

Submitted to the Board of University Studies of the Johns Hopkins University in Conformity with the Requirements for the Degree of Doctor of Philosophy.

BY

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THE VAPOR PRESSURE OF AQUEOUS SOLUTIONS OF POTASSIUM CHLORIDE. AT 20° C.

While continuing the study of the vapor pressure of aqueous solutions by the improved static method devised by Frazer and Lovelace,[1] it was found that the process originally employed for the removal of air from the solutions was unsatisfactory both from the standpoint of completeness and of the time consumed. To overcome these objections it seemed desirable to prepare the solutions in vacuo, i.e., mix the air free constituents in a vacuum, or else boil the solutions untill all air is expelled, sealing the container while filled with steam. On account of the instability of some solutions at boiling temperatures, it was decided to develop the first method mentioned above which is herein later described in detail. The work with solutions thus prepared so nearly air free has revealed the possibility that the former measurements may be unreliable due to traces of air in the solutions. While the statement is made in the reports of former work that no readings of the vapor pressure lowering were made until the McLeod gauge showed a residual air pressure of less than 0.0001 mm after a 24-hour expansion, error has very probably been made in reading the gauge. The

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1. J. Am. Chem. Soc. 36, 2439 (1914).
   Ibid 38, 515 (1916).

usual procedure in making air tests was to allow the vapor of the solution to expand into a previously evacuated bulb for a period of 24 hours. The solution was then trapped off and the water vapor absorbed by phosphorous pentoxide. A period of over night was generally allowed for the absorption and the residual air pressure was read the next morning on the McLeod gauge. Now, not only is the water vapor absorbed in this time, but also a considerable amount of the air is adsorbed, presumably by the pentoxide and the walls of the system. It has been repeatedly demonstrated in the course of this work that fifteen to twenty minutes is ample for the absorption of the water vapor and the reading on the McLeod gauge at the end of this time is a correct measure of the amount of air present. In view of these facts it was deemed advisable to repeat the measurements on potassium chloride solutions. The work was also extended into more dilute and more concentrated solutions.

APPARATUS.

The apparatus used in this work was essentially the same as that described in a former article.[1] No changes have been made in the bath design or thermoregulation. An extra trap has been placed in the system[2]

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1. J. Am. Chem. Soc., 38, 515

2. ibid 38, 521, fig. 3.

connecting a point to the right of trap number 11 with a point to the right of trap number 5, thus enabling one solution to be balanced against another in the Rayleigh manometer. Such a trap was desirable not only for checking readings, but as the flexibility of the manometer was limited, it became necessary to devise this means for reading concentrated solutions. For example, a 1.5 M solution was read against the solvent, then a 3.0 M solution against the 1.5 M. This 3.0 M solution was left in the bath and higher concentrations read against it.

A more powerful telescope for reading the deflections, s, and a silver millimeter scale have been installed. The difficulties in illuminating a metallic scale had forced the use of a paper scale hitherto, but a frosted glass plate set in an ordinary photographer's dark room lantern equipped with a tungsten lamp was found to give excellent illumination of the metallic scale.

EXPERIMENTAL.

The potassium chloride used in this investigation was the best obtainable stock with guaranteed analysis, and was recrystalized from freshly distilled water, using centrifugal drainage. Careful tests for impurities were negative, except for water. No special precautions were taken for drying the salt except that used for making standards for analysis of solutions in the interferometer. This portion

fig. 1

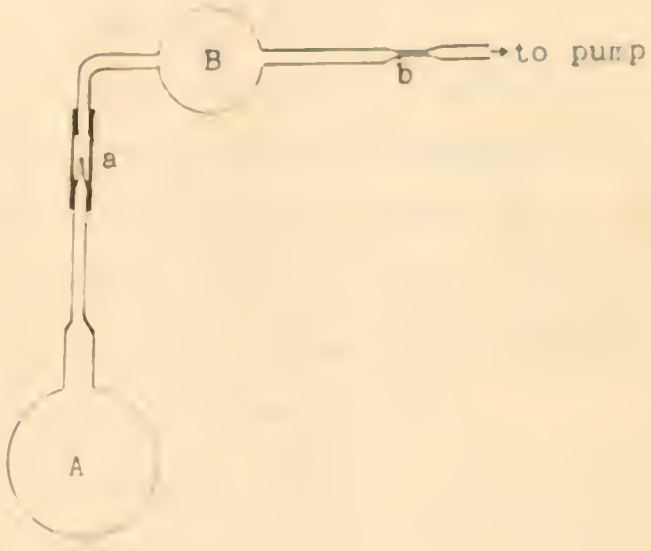

fig. 2

fig. 3

was dried to constant weight in an air bath at 300 degrees. To illustrate the difficulty of drying potassium chloride, a sample dried over night at 150 degrees and then over calcium chloride for 16 days was found to still contain several tenths of a percent of water.

Before introducing a solution into the bath, the entire system was evacuated by intermittent pumpings for a period of 24 to 36 hours. Solutions were made up to approximate strengths, introduced into the bath, read and analyzed after coming from the bath. The method of making up and introducing the solutions is as follows:

A round bottom pyrex flask A, figure 1, with a tube of 7 mm internal diameter sealed on to the neck is filled with water. A constriction is drawn at a and a piece of rubber tubing is attached to the end of the tube. The water is then vigorously boiled for 30-40 minutes allowing a free escape of steam. When about 300 cc of water remain, the rubber tube is pinched shut, the flask removed instantly from the flame and sealed off at the constriction. When the sealed end is inclined downward the entrapped bubble of vapor must close completely and with a metallic click, or the water is rejected as not being sufficiently air free.

The weight of the water having been determined to 0.1 gram, an amount of solute corresponding to this amount

of water for a desired concentration is then weighed into a flask B, figure 2, by means of a short funnel attached with a rubber tube. A file mark is placed on the tip a, and flasks A and B are connected with a rubber tube as shown in figure 2. The other end of B is attached to the pump and after several hours exhaustion is sealed off at b. Heating B in a steam bath facilitates the removal of adsorbed air on the solute. The tip a is then broken in the rubber tube and solvent and solute mixed.

After mixing, the rubber tube is pinched shut, the flask A is removed and a capillary pipette p, figure 3, inserted in its place. To the other end of B a mercury reservoir, partly filled, is attached and held horizontally. The reservoir is evacuated for a few minutes with the oil pump, then righted and the tube around b is carefully filled with mercury. The tip b is next broken, the solution is forced though the pipette and allowed to waste until all air bubbles have been swept from the pipette, then it is directed up through the mercury column into the evacuated system, F, G or H. No trouble is experienced with air leaking in at the rubber connection if a tight fitting tube is selected and it is tied on with soft iron wire twisted tight with a pair of pliers.

With careful manipulation, the solutions thus introduced showed negligible air in tests made after four to six twelve-hour expansions. The concentrated solutions did not come air free quite so rapidly, due doubtless to the difficulty in pumping off the adsorbed air on the solid salt during the preparation of the solution.

After a solution showed negligible air, readings were taken on the manometer until about five consecutive concordant readings extending over a period of two or more days were obtained. The procedure was to take a zero point with both limbs of the manometer connected with the same system, generally that one containing the solvent and its vapor. Then immediately the traps were adjusted for reading the lowering of a solution, and after allowing ten or fifteen minutes for the establishment of equilibrium, at least three settings were taken on the manometer. No reading was regarded reliable unless the zero point was afterwards checked within the limit of accuracy of setting the manometer. Owing to the unfortunate situation of the laboratory near heavy street and railway traffic the zero point was not always checked. If then on returning to the solution the reading of the solution could be checked, these readings with the new zero point were regarded as reliable.

Under good conditions the manometer was easily set to a tenth of a millimeter. As one millimeter on the scale for the present mounting of the telescope amounts to 0.00511 mm actual difference in level of the meniscii in the manometer, this indicates an accuracy of approximately 0.0005 mm in setting. A study of the deflections recorded herein will show that seldom ever did the measurement of the lowering of the vapor pressure of a solution vary as much as 0.001 mm over a period of several days.

Owing to the fact that the solvent was allowed to stand in the bath for several months at the time, there was a possibility of its extracting alkali from the glass. Not only was the solvent carefully tested for soluble matter on coming from the bath, but during the course of the work fresh solvent was introduced into one of the systems and read against the original solvent. In no case were the findings sufficient to change the results.

The statement in former articles that exact regulation of room temperature is unnecessary was rigorously tested out and confirmed. It is only necessary to avoid air currents and sudden changes of temperature in the room.

CALCULATIONS

The vapor pressure lowerings were calculated from the observations by means of the following equations:

(1) $h = d \sin\theta$

(2) $s = D \tan 2\theta$

in which, d = distance between the points in the manometer,

D = distance from scale to mirror on manometer,

s = the deflection read on the scale,

h = the pressure difference in the limbs of manometer,

θ = angle through which the manometer is rotated

Combining (1) and (2),

$$h = \frac{ds}{2D} \frac{\sin\theta}{\frac{1}{2}\tan 2\theta}.$$

For values of θ up to 1 degree, the expression, $\sin\theta / \frac{1}{2}\tan 2\theta$, may be put equal to unity, and the formula becomes,

$$h = \frac{ds}{2D}.$$

Since d/2D is constant, the expression simplifies to

$$h = ks.$$

This formula has been used in calculating the lowering of dilute solutions, but above 0.7 M where its use involves a certain small error, use has been made of (1) and (2) combined thus:

$$h = d \sin \frac{\tan^{-1} \frac{s}{D}}{2}.$$

Values of h obtained in mm of Hg at room temperature (24°) are

corrected to Hg at 0°, and recorded in Table 1 under $p_o - p_1$.

The vapor pressure lowerings for solutions of mannite investigated by this method[1] have been found to follow Raoult's law very closely. Using them as a basis, the calculation of the percentage ionization of dilute solutions of potassium chloride has been attempted. If the concentration-lowering curve for mannite be a straight line it makes no difference whether ionization be calculated from the ratio of the lowering of a given concentration of potassium chloride to the lowering of the same concentration of mannite, or from the ratio of the concentrations giving the same lowering. Use of the former,

$$\frac{\text{Lowering of KCl}}{\text{Lowering of Mannite}} - 1 = \% \text{ Ionization},$$

has been made in these calculations, as interpolations over very short ranges of concentration have been necessary to express the percentage ionization at even concentrations.

The vapor pressure of a solution may be calculated from its freezing point. The equation[2] connecting the solvent mol fraction $N/N+n$ with the lowering of freezing point, Δt, is:

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1. T H Rogers, Doctor's Dissertation, Hopkins, 1917
2. Washburn, Principles of Physical Chem

$$(1)\quad \log_{10}\frac{N}{N+n} = -\frac{0.4343\ L_F}{R\ T_{F_o}}\ \frac{\Delta t_F}{T_F},$$

where L_F = latent heat of fusion of 1 mol of solvent,

T_{F_o} = absolute freezing point of the solvent, and

T_F = absolute freezing point of the solution.

From Raoult's law we get

$$(2)\quad \frac{N}{N+n} = \frac{p_1}{p_o}$$

where p_1 = vapor pressure of the solution

and p_o = vapor pressure of pure solvent. It follows that

$$(3)\quad \log_{10}\frac{N}{N+n} = \log_{10}\frac{p_1}{p_o}$$

Equating (1) and (3) we get

$$(4)\quad \log_{10}\frac{p_1}{p_o} = -\frac{0.4343\ L_F}{R\ T_{F_o}}\ \frac{\Delta t_F}{T_F}, \text{ or}$$

$$(5)\quad \log_{10}p_1 = \log_{10}p_o - k\frac{\Delta t_F}{T}.$$

We may employ this equation to calculate the vapor pressure of a solution at its freezing point. If von Babo's law holds

$$\left(\frac{p_1}{p_o}\right)_{0^\circ} = \left(\frac{p_1}{p_o}\right)_{20}$$

Then substituting the vapor pressure of the pure solvent at 20° for p_o in (5), p_1 comes out to be the vapor pressure of the solution at 20°.

ANALYSIS OF SOLUTIONS.

A Zeiss interferometer was used to analyze the solutions after they were taken from the bath. A twenty millimeter cell was calibrated over the range of KCl. In order that any error in the determination of the value of the screw divisions around any given concentration may be negligible, it was aimed always in the final analysis to have the standard approximately the same concentration as that of the unknown solution. This often involved the use of a second standard made up to the strength indicated by the first analysis.

To insure confidence in the ability to match the bands in the interferometer, weighed portions of the solutions were occasionally evaporated to dryness in a platinum dish and the residue dried to constant weight at 300 degrees. In this way check values of the analyses on the interferometer were obtained with no difficulty.

The concentration of all solutions is expressed in mols per 1000 grams of solvent, using 74.56 as the molecular weight of KCl

DATA

The Vapor Pressure Lowerings
of Twenty Solutions of
Potassium Chloride
at 20 Degrees.

0.0498 M KCl

Date	Zero	Reading	Zero	Reading	Deflection
3/10/17	282.9	288.6			
	282.9	288.65			
		288.55	282.85		
		288.6	282.9		5.71
3/10/17	282.1	287.9			
	282.1	287.9	282.1		
		287.9	282.15		5.79
3/11/17	281.3	287.0			
	281.25	287.05	281.25		
	281.3	287.1	281.35		
		287.05	281.3		5.76
3/12/17	282.0	287.8			
		287.8	282.05		
		287.8	282.05		5.77
3/12/17	283.0	288.8			
	283.05	288.8			
	283.0	288.75			
		288.75	283.0		5.76
				Average Deflection	5.76 mm

D = 3804 mm

d = 38.90 mm

k = 0.005113

0.0704 M KCl

Date	Zero	Reading	Zero	Reading	Deflection
3/10/17	282.85	290.85	282.8		
	282.9	290.85	282.75		
		290.85	282.8		8.03
3/10/17	282.1	290.15			
	282.15	290.1	282.05		
		290.05	282.1		8.00
3/11/17	281.25	289.3			
	281.35	289.35			
	281.3	289.3	281.3		8.02
3/12/17	281.95	290.0			
	281.95	289.95			
		290.0	282.0		8.01
			Average Deflection		8.02 mm

D = 3804 mm

d = 38.90 mm

k = 0.005113

0.0997 M KCl

Date	Zero	Reading	Zero	Reading	Deflection
3/1/17	283.8	295.1			
	283.85	295.05	283.85		
		295.05	283.8		11.25
3/2/17	283.75	295.05			
	283.75	294.95			
		295.0	283.75		11.25
3/2/17		293.15			
		293.1	281.9	293.1	
		293.1	281.9	293.2	
		293.1	281.9	293.1	11.22
3/2/17	281.9	293.15			
	281.9	293.05	281.95		
		293.1	281.95		
		293.15	281.95		11.18
3/3/17	283.75	295.05			
	283.8	294.95			
		295.1	283.75		
		295.05	283.8		11.27
3/3/17	283.75	295.15	283.85		
	283.8	295.1	283.9		
		295.1	283.85		11.29
3/3/17	283.85	295.05			
	283.8	295.1	283.8		
		295.05	283.75		11.27
3/3/17	283.0	294.2			
	283.0	294.25	283.95		
		294.2	283.95		11.26
			Average Deflection		11.25 mm

D = 3804 mm

d = 78.90 k = 0.005117

0.2013 N KCl

Date	Zero	Reading	Zero	Reading	Deflection
4/11/17	277.95	300.25			
	277.95	300.2	277.85		
	277.95	300.35	277.85		
		300.2	277.95		
		300.25	277.95		22.32
4/11/17	277.45	299.9			
	277.5	299.9	277.55		
		299.85	277.5		22.38
4/11/17	276.6	298.8			
	276.6	298.8	276.65		
		298.8	276.6		22.19
4/12/17	284.85	307.2			
	284.85	307.15	284.95		
		307.2	284.9		
		307.2	284.85		22.31
4/12/17	284.9	307.1			
	284.9	307.2			
		307.15	284.85		22.27
4/13/17	285.65	307.9			
	285.65	307.9			
		307.9	285.65		22.25

Average Deflection 22.29 mm

D = 3801 mm

d = 38.90 mm

k = 0.005117

0.2985 N KCl

Date	Zero	Reading	Zero	Reading	Deflection
1/23/17	290.5	323.45			
	290.6	323.4			
	290.4	323.3	290.5		
	290.5	323.35	290.55		32.87
1/23/17	290.5	323.4	290.65		
	290.55	323.35	290.55		
		323.4	290.55		32.82
1/23/17	290.0	322.85			
	289.95	322.9			
		322.8	290.0		32.87
1/24/17	290.65	323.55	290.55		
	290.65	323.5	290.8		
		323.55	290.7		32.86
1/24/17	290.15	323.0			
	290.15	322.95	290.05		
		323.0	290.05		32.88
			Average Deflection,		32.86 mm

D = 3807. mm

d = 38.90 mm

k = 0.005108.

0.3855 M KCl

Date	Zero	Reading	Zero	Reading	Deflection
1/13/17	291.0	333.1			
	291.0	333.15	290.9		
		333.05	290.9		42.15
1/16/17		332.9	290.8		
		332.9	290.7		
		332.9	(290.9)		
			290.75	332.9	
			290.8	332.85	42.13
1/16/17	291.0	333.15			
	291.0	333.15			
	291.0	333.15	291.0		42.15
1/16/17	290.85	333.0			
	290.9	333.0			
		333.0	290.85		42.13
1/17/17	291.5	333.6			
	291.5	333.7			
		333.7	291.5		42.17
			Average Deflection		42.15 mm

D = 3807. mm

d = 38.90 mm

k = 0.005109

0.4973 M KCl

Date	Zero	Reading	Zero	Reading	Deflection
1/23/17	290.65	345.0			
	290.55	345.0	290.6		
	290.55	345.0	290.5		54.43
1/23/17	290.0	344.5			
		344.55	290.05		
		344.5	290.0		54.50
1/24/17	290.55	345.1			
	290.8	345.15	290.7		
	290.7	345.1	290.7		54.43
1/24/17		345.3			
		345.25			
		345.35	290.85		
		345.2	290.8	345.25	
		345.2	290.9	345.35	54.42
1/24/17	290.2	344.6			
	290.2	344.7	290.15		
		344.7	290.15		54.49

Average Deflection 54.45 mm

D = 3807. mm

d = 38.90 mm k = 0.005109

0.6000 N KCl

Date	Zero	Reading	Zero	Reading	Deflection
1/31/17	290.05	355.8			
	290.1	355.85	290.0		
		355.9	289.95		
		355.9	289.95		65.85
1/31/17	290.0	355.9			
	289.95	355.85			
	289.95	355.75	290.0		65.85
1/31/17	290.05	355.9			
	290.1	355.9	290.0		
		355.85	290.0		65.84
2/1/17	290.4	356.25			
	290.45	356.15			
	290.4	356.15	290.5		
	290.5	356.2	290.5		65.73
2/1/17	290.8	356.5			
	290.7	356.4	290.75		
	290.7	356.5	290.8		65.72
2/1/17		356.8			
		356.8			
		356.8	291.05		
			291.0	356.8	
			291.0	356.85	65.79

D = 3807 mm Average Deflection 65.80 mm

d = 38.90 mm

k = 0.005109

0.6995 M KCl

Date	Zero	Reading	Zero	Reading	Deflection
1/20/17	283.0	359.55			
	283.0	359.5			
		359.7			
		359.7	283.0		
		359.65	283.0		76.62
1/20/17	283.0	359.55			
	283.0	359.75			
		359.65			
		359.65	282.95		76.67
1/20/17	281.9	358.45			
	281.85	358.5			
		358.5	281.85		76.61
1/21/17	282.1	358.7			
	282.05	358.7	282.15		
		358.7	282.15		76.58
1/21/17	281.4				
	281.4	357.95	281.3		
	281.35	357.95	281.35		
	281.5	357.95	281.35		76.57
1/22/17		358.7	282.2		
		358.8	282.15	358.75	
		358.7	282.2	358.7	76.55

Average Deflection 76.60 mm

D = 3804. mm

d = 38.90 mm

k = 0.005113

0.7958 N KCl

Date	Zero	Reading	Zero	Reading	Deflection
1/30/17	289.8	376.6			
	289.85	376.6	289.85		
		376.55	289.8		86.75
1/30/17	289.2	376.0			
	289.2	375.9	289.15		
		375.95	289.15		86.78
1/30/17	289.25	376.05			
	289.3	376.05			
		376.05	289.25		86.78
1/31/17	290.5	377.2	290.35		
	290.5	377.15	(290.2)		
		377.1	290.4		
		377.1	290.3		86.73
1/31/17	290.8	377.5			
	290.8	377.55			
		377.4			
		377.6			
		377.5	290.8		86.71
1/31/17	290.0	376.8			
	290.0	376.8			
		376.85	290.0		86.82
			General Average		86.76 mm

D = 3807. mm

d = 30.90 mm

k = 0.005109

0.9968 M KCl

Date	Zero	Reading	Zero	Reading	Deflection
2/17/17	287.2	395.75			
	287.2	395.85			
		395.8	287.15		
		395.8	287.25		108.60
2/17/17	287.2	395.95			
	287.3	395.9	287.2		
		395.9	287.25		108.68
2/17/17		391.65			
		391.7	283.25		
		391.8	283.2	391.7	
		391.75	283.2	391.75	108.50
2/18/17	285.15				
	285.15	393.7			
	285.1	393.7			
	285.2	393.75	285.1		108.58
2/18/17	285.0	393.5	284.9		
	285.05	393.45	285.0		
		393.55	284.95		108.52
2/20/17		392.2	283.7		
		392.25	283.6	392.2	
		392.2	283.7	392.2	108.56
			Average Deflection		108.57 mm

D = 3804. mm

d = 38.90 mm

k = 0.005113

1.2461 M KCl

Date	Zero	Reading	Zero	Reading	Deflection
3/29/17	282.2	417.9			
	282.2	417.9	282.2		
		417.85	282.2		135.68
3/29/17	281.3	416.95			
	281.3	417.0	281.2		
		416.95	281.3		135.69
3/30/17	282.5	418.2			
	282.5	418.1	282.5		
		418.1	282.5		135.63
3/30/17	281.65	417.3			
	281.6	417.15			
		417.15	281.5		
		417.2	281.5		135.64
3/31/17	281.9	417.65			
	281.9	417.7	281.95		
		417.7	281.9		135.77
3/31/17	281.85	417.6			
	281.85	417.6	281.9		
	281.85	417.65	281.85		135.76
			Average Deflection		135.69 mm

D = 3804. mm

d = 38.90 mm

k = 0.005113

1.5099 M KCl

Date	Zero	Reading	Zero	Reading	Deflection
4/25/17	283.2	447.65			
	283.2	447.85	283.15		
	283.25	447.8	283.15		164.64
4/25/17	282.9	447.5			
	282.9	447.5			
		447.55	282.85		
		447.5	282.85		164.63
4/26/17	281.9	446.6			
	281.85	446.6			
	281.85	446.5	281.9		164.70
4/26/17	282.0	446.7			
	282.0	446.65			
		446.65	282.0		164.67
4/26/17	281.45	446.0			
	281.45	446.05			
		446.05	281.45		164.60

Average Deflection 164.65 mm

D = 3801. mm

d = 38.90 mm

k = 0.005117

1.7072 M KCl

Readings against 0.2013 M KCl.

Date	Zero	Reading	Zero	Reading	Deflection
4/10/17	277.95	442.0			
	277.95	441.95	278.0		
	277.9	441.9	278.0		163.99
4/10/17	276.95	440.85			
	277.0	440.9	276.95		
		440.85	276.95		163.91
4/11/17		441.15			
		441.1	277.2		
		441.05	277.15	441.1	
		441.1	277.2	441.15	163.93
4/12/17	284.95	448.85			
	284.9	448.7			
	284.85	448.75			
		448.7	284.85		
		448.8	284.9		
		448.7	284.85		163.87
4/12/17	284.85	448.8			
		448.75	284.85		
		448.75	284.85		163.92

Average Deflection 163.92 mm

Deflection of 0.2013 M (q.v.) 22.29 mm

D = 3801. mm

d = 38.90 mm

k = 0.005117

1.9938 M KCl

Readings against 0.6995 M KCl

Date	Zero	Reading	Zero	Reading	Deflection
3/20/17	282.95	424.0			
		423.95	282.9		
		423.95	282.95		141.04
3/20/17	281.85	422.95			
		422.9	281.8		
		422.9	281.85		141.09
3/21/17	282.15	423.35	282.25		
	282.15	423.3	282.25		
		423.3	282.25		141.11
3/21/17	281.3	422.4			
	281.35	422.35			
	281.35	422.4			
		422.4	281.35		
		422.35	281.3		141.05
3/22/17	282.2	423.2	282.05		
	282.15	423.3	282.2		
	282.2	423.2	282.2		141.06

Average Deflection 141.07 mm

Deflection of 0.6995 M (q.v.) 76.60 mm

D = 3804. mm

d = 38.50 mm

k = 0.005113

2.2450 M KCl

Readings against 1.2461 M KCl

Date	Zero	Reading	Zero	Reading	Deflection
3/29/17	282.2	392.0			
	282.2	391.95	282.15		
		391.95	282.15		109.80
3/29/17	281.2	391.1			
	281.3	391.1	281.15		
		391.05	281.15		109.88
3/30/17	282.5	392.3			
	282.5	392.35			
		392.45	282.65		
		392.5	282.6		
		392.5	282.7		109.83
3/30/17	281.5	391.45			
	281.5	391.35			
		391.3			
		391.35	281.45		109.88
3/31/17	281.95	391.8			
	281.9	391.8	282.0		
		391.85	282.0		109.86
3/31/17	281.9	391.7			
	281.85	391.7	281.8		
		391.75	281.85		109.87
			Average Deflection		109.85mm
			Deflection of 1.2461 M(a.v.)		135.69mm

D = 3804 mm

d = 38.90 mm

k = 0.005113

2.4916 M KCl

Readings against 0.9968 M KCl

Date	Zero	Reading	Zero	Reading	Deflection
2/20/17	282.6	447.0			
	282.6	446.95	282.5		
		446.95	282.55		164.41
2/21/17	283.5	447.95			
	283.55	447.95			
		447.95	283.5		164.43
2/21/17	283.5	448.0			
	283.45	447.9			
		448.1	283.55		
		448.0	283.55		164.49
2/21/17	283.45	448.0			
	283.5	447.95	283.6		
		447.95	283.5		164.46
2/21/17	282.9	447.3			
	282.9	447.35			
		447.3	282.85		
		447.2	282.85		164.41
2/22/17	281.5	445.9			
	281.35	445.9	281.5		
	281.4	446.0	281.5		164.48

Average Deflection 164.45mm

Deflection of 0.9968 M(i.v.) 164.57mm

D = 3804. mm

d = 38.90 mm

k = 0.005113

3.0017 M KCl

Readings against 1.5099 M KCl

Date	Zero	Reading	Zero	Reading	Deflection
4/23/17	284.9	451.05			
	284.85	451.0			
	284.85	451.05	284.85		166.17
4/23/17	283.7	449.95			
		449.95	283.8		
		450.0	283.8		166.20
4/25/17	281.95	448.1			
	281.95	448.15	281.9		
		448.1	281.9		166.20
4/25/17	283.15	449.3			
	283.15	449.4			
		449.4	283.15		166.22
4/25/17	282.85	449.05			
	282.85	449.0			
		449.05	282.8		166.20
4/26/17	281.9	448.1			
		448.15	281.95		
		448.1	281.9		166.20

Average Deflection 166.20mm

Deflection of 1.5099 M(q.v.) 164.65mm

D = 3801 mm

d = 38.90 mm

k = 0.005117

3.5783 M KCl

Readings against 3.0017 M KCl

Date	Zero	Reading	Zero	Reading	Deflection
5/10/17	301.0	235.05	301.1		
	301.0	235.1	301.1		
		235.1	301.05		65.97
5/10/17	301.05	235.0	301.0		
	301.05	235.0	301.0		66.02
		235.0			
5/10/17	281.0				
	281.0	215.05			
		215.0	281.05		
		215.0	281.05		66.00
5/11/17	301.0	235.0			
	300.95	235.0	301.0		
		235.05	301.0		65.97
5/11/17	300.85	234.85			
	300.9	234.9	300.95		
		234.9	300.95		66.03

Average Deflection 66.00 mm

Deflection of 3.0017 M (a.v.) { 166.20 mm / 164.65 mm

D = 3801 mm

d = 38.90 mm

k = 0.005117

4.0070 M KCl

Readings against 3.0017 M KCl

Date	Zero	Reading	Zero	Reading	Deflection
5/10/17	301.1	185.3			
	301.1	185.3			
	301.05	185.2	301.05		115.80
5/10/17	301.05	185.3			
	301.05	185.25			
		185.2	301.0		
		185.2	301.0		115.78
5/11/17	301.0	185.2			
	300.95	185.25	301.0		
		185.2	301.0		115.77
5/11/17	300.85	185.1			
	300.9	185.05	300.95		
		185.05	300.95		115.84
		Avorage Deflection			115.80 mm
		Deflection of 3.0017 M (q.v.)			166.20 mm 164.65 mm

D = 3801.mm d = 38.90 mm

k = 0.005117

SUMMARY OF DATA

Table 1

G = grams of KCl per 1000 grams of solvent
M = mols (74.56) per 1000 grams of solvent
s = scale deflection
D = distance from mirror to scale
k = constant employed for small deflections
$p_o - p_1$ = lowering in mm of Hg (Hg correc. to 0° C.)

G	M	s	D	$kx10^6$	h	$p_o - p_1$	$\frac{p_o - p_1}{M}$
3.7132	0.0498	5.76	3804	5113	0.0294	0.0293	0.5888
5.2490	0.0704	8.02	3804	5113	0.0410	0.0408	0.5799
7.4339	0.0997	11.25	3804	5113	0.0575	0.0573	0.5744
15.009	0.2013	22.29	3801	5117	0.1141	0.1136	0.5641
22.256	0.2985	32.86	3807	5109	0.1679	0.1672	0.5600
28.743	0.3855	42.15	3807	5109	0.2153	0.2144	0.5562
37.079	0.4973	54.45	3807	5109	0.2782	0.2770	0.5569
44.736	0.6000	65.80	3807	5109	0.3362	0.3347	0.5579
52.156	0.6995	76.60	3804	5113	0.3916	0.3899	0.5573
59.335	0.7958	86.76	3807	5109	0.4432	0.4412	0.5544
74.322	0.9968	108.57	3804	5113	0.5549	0.5525	0.5543
92.912	1.2461	135.69	3804	5113	0.6934	0.6904	0.5540
112.58	1.5099	164.65	3801	5117	0.8420	0.8383	0.5552
127.29	1.7072	163.92 22.29	3801	5117	0.9523	0.9482	0.5554
148.66	1.9938	141.07 76.60	3804	5113	1.1125	1.1077	0.5556
167.39	2.2450	109.85 135.69	3804	5113	1.2546	1.2492	0.5564
185.775	2.4916	164.45 108.57	3804	5113	1.3952	1.3893	0.5576
223.81	3.0017	166.20 164.65	3801	5117	1.6918	1.6844	0.5611
266.80	3.5783	66.00 166.20 164.65	3801	5117	2.0395	2.0307	0.5647
298.765	4.0070	115.80 166.20 164.65	3801	5117	2.2841	2.2741	0.5675

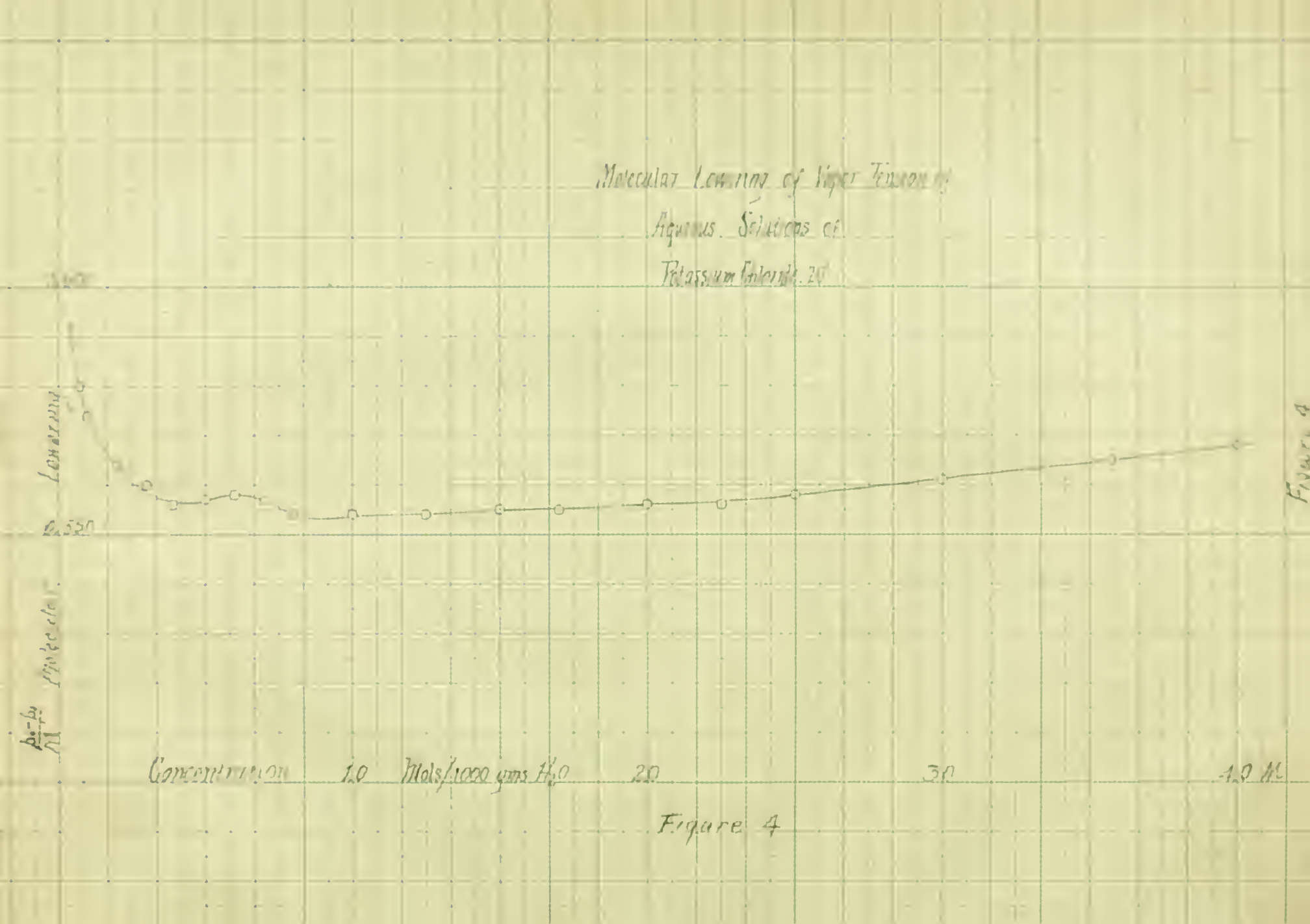
Molecular Lowering of Vapor Tension of
Aqueous Solutions of
Potassium Chloride. 25°
Lowering
0.520
Concentration
1.0 Mols/1000 gms H2O
2.0
3.0
4.0 M

Figure 4

DISCUSSION OF RESULTS.

1. Molecular Lowering Curve.

The variation in lowering of vapor pressure with concentration is best seen when $p_o - p_1/M$ is plotted against concentration. See figure 4. Solutions below 0.4 M behave with respect to lowering of vapor pressure as would be expected of a solution of an ionizing salt. In the region of the 0.6 M there is a distinct maximum which, considering the smoothness of the curve over other regions, we cannot attribute to experimental error. The minimum at 0.4 M has been observed in the previous measurements of potassium chloride as reference to Table 2 will show. Irregular lowerings for solutions of mannite investigated by this method have been indicated between 0.4 M and 0.6 M.

It does not seem reasonable to ascribe this irregular molecular lowering to changes in the degree of hydration, since it is generally conceded that potassium chloride is nearly an ideal solute and does not combine with water in a chemical sense. The explanation is probably to be found in the complex highly associated solvent employed. It is believed that water consists of three different molecular species in an equilibrium

which undergoes marked change with varying temperature and pressure. According to the theory of La Place, the fundamental properties of any liquid depend on the enormous forces between the molecules producing what is known as molecular or inner pressure which opposes any increase in the volume of the liquid. The process of solution may be regarded as a means of expanding the liquid without the application of heat. The molecules of the solute are dispersed between the molecules of the liquid thereby forcing them apart and expanding the liquid. A gas is expanded by changing the external pressure--we employ the solute as a means of applying the expanding pressure within the body of the liquid itself. The physical properties of a solution, such as vapor pressure, boiling point, freezing point etc., are merely the properties of the expanded solvent. As we dissolve more and more potassium chloride in water, the inner pressure becomes greater and greater, the equilibrium between the different molecular species of water shifts, and it seems quite reasonable to assure that the vapor pressure would show irregularities at any point where a marked shift from one form to another took place.

The marked decrease in the viscosity of water with rise in temperature is attributed to the dissociation of the complex water molecules. That the molecular complexity of water is simplified by the presence of a dissolved substance seems to be borne out in the observations of relative

viscosity of solutions of certain salts, of which potassium chloride is one, where a decrease in the viscosity of water is brought about by the addition of slight amounts of the salt. This phenomenon has been called "negative viscosity." Especially is such behaviour true at the lower temperatures of water where its molecular complexity is greatest. Ranken and Taylor[1] state that the relative viscosity curve of such solutions contains at least one minimum at a point along the concentration axis which is determined by the nature of the dissolved substance and the temperature. At such a point, relative fluidity is a maximum. The water particles have the greatest freedom of motion, their escaping tendency has been increased, the vapor pressure of the solution is consequently greater, and therefore the lowering will be diminished at such a point. Viscosity measurements of potassium chloride solutions at 20 degrees are not available, but reference to values at adjacent temperatures given in Table 3 and plotted in figure 5 shows that the molecular lowering curve follows the relative viscosity curve in a very striking manner. Getman[2] finds a minimum in the absolute viscosity curve of

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1. Proc. Roy. Soc. Edin., 45, 397

2. J. Am. Chem. Soc., 30, 721 (1908); J. Phys. Chem. Phys., 5, 344 (1907)

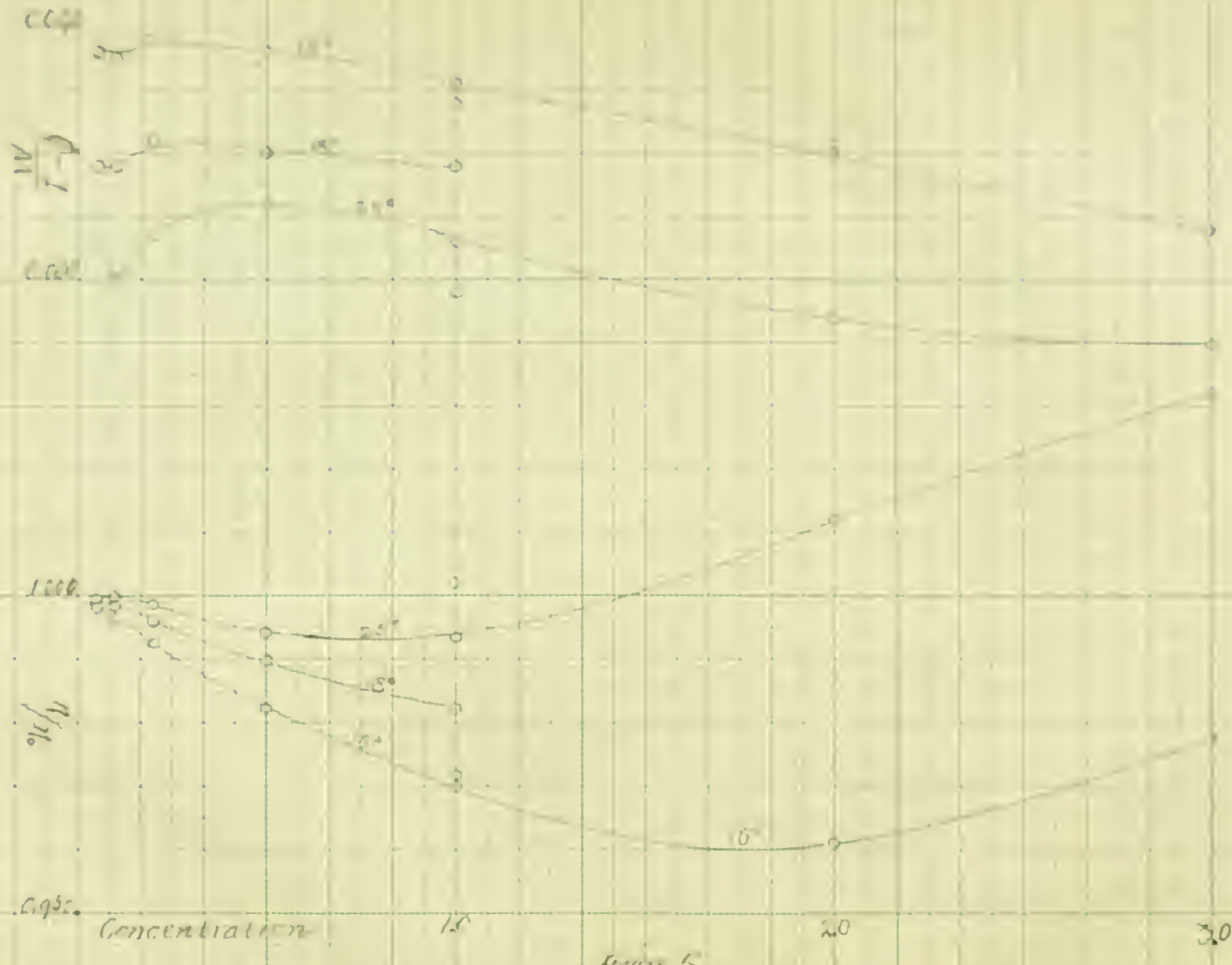

Figure 5

Table 2.

Concentration Mols per 1000 gms water	Molecular Lowering Former Results	Recent Results
0.2	0.550	0.564
0.4	0.542	0.556
0.6	0.548	0.555
0.8	0.547	0.554
1.0	0.547	0.554
1.2	0.552	0.554
1.5	0.550	0.555
2.0	0.551	0.556

Comparison of Recent Results of Vapor Pressure Lowering of Potassium Chloride Solutions with Former Results.

Table 3

Conc	Rel Visc η/η_0	Rel Fluidity ϕ	$\frac{\phi - 1}{M}$	Rel Visc η/η_0	Rel Fluidity ϕ	$\frac{\phi - 1}{M}$
	15°	Ranken and Taylor[1]		25°		
0.05	0.9982	1.0018	0.036	0.9995	1.0005	0.010
0.1	0.9965	1.0035	0.035	1.0000	1.0000	0.000
0.2	0.9925	1.0075	0.038	0.9985	1.0015	0.007
0.5	0.9822	1.0178	0.036	0.994	1.0060	0.012
1.0	0.9695	1.0305	0.031	0.9975	1.0065	0.006
1.0	0.9719	1.0281	0.028	1.002	0.998	-0.002
2.0	0.961	1.039	0.020	1.012	0.988	-0.006
3.0	0.9766	1.0234	0.008	1.032	0.968	-0.010
	18°	Gruneisen[2]				
0.05	0.9991	1.0009	0.018			
0.1	0.9982	1.0018	0.018			
0.2	0.9959	1.0041	0.022			
0.5	0.9898	1.0102	0.020			
1.0	0.982	1.0180	0.018			

Relative Viscosity of Potassium Chloride Solutions at 15°, 18°, 25°.

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1. loc. cit., and reference there to former article

2. Wiss. Abh. der Phys. Tech. Reichsanstalt, 4, 339.

potassium chloride solutions at 18 degrees at a point about 1.0 M. He records only one value in the "negative viscosity" region of the curve.

Speculating to some extent, we may review the entire molecular lowering curve in the following manner: In dilute solutions the lowering comes down just as would be expected with decreasing ionization. But around 0.4 M where a slight minimum occurs in the lowering the influence of fluidity predominates over any ionization influences,—the values of $\Phi - 1 / M$, the ratio of the increase of fluidity over that of water to the mols of dissolved substance, tends to a maximum in just this region. At about 0.6 M, ionization influences recover, and the curve slopes downward again. It would be interesting to investigate solutions of sodium chloride which do not exhibit "negative viscosity," and see if this break in the lowering curve is absent. At about 1.0 M we may imagine that the water molecules are shifted to their simplest form, and if the volume of the potassium molecules and ions be greater than the volume of the water molecules, then the further addition of potassium chloride

serves only to increase the viscosity of the solution. That is to say, the fluidity decreases in a linear manner, and the vapor pressure is affected in the same manner. The idea of hydration is not to be disparaged, especially in the concentrated solutions would its influences be noticeable, not only in increasing the volume of the potassium chloride molecules and ions, but also in removing the solventfrom its role.

There are no measurements of the vapor pressure of potassium chloride solutions at 20 degrees by other methods available for comparison with the results obtained in this investigation. Table 2 gives the former values by this same method.[1] Complete reroval of air from the solutions was not obtained in the former work.

2. Calculation of Vapor Pressure Lowering from Freezing Point Lowering.

In calculating the vapor pressure of solutions at 20 degrees from freezing point observations the values given by Noyes and Falk[2] as the weighted mean of all

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1. Lovelace, Frazer & Miller, J. Am. Chem. Soc., 35, 527

2. J. Am. Chem. Soc., 32, 1020 (1910)

recent reliable freezing point work were first employed. Table 4 contains these values and the lowerings calculated therefrom are compared with those observed in the present investigation. In extending the calculations to concentrated solutions, the freezing point data of Roloff[1] seemed to be the best available work. While not included in the weighted means of Noyes and Falk it shows very close agreement where the concentrations overlap. The calculations are given in Table 5. Concentrations in both tables are expressed in mols per 1000 grams of solvent.

The difference between calculated and observed values is about 1--3 %. This might appear to be due to error when we consider that in the freezing point determination the thermometer was read to 0.001 degrees, and that a mercury column was measured to 0.001 mm in the vapor pressure measurement -- two delicate experimental operations. But the greatest part of the error involved lies in the assumption upon which the calculation was based, viz., that von Babo's law held. If p_o/p_1 is independent of temperature as the law states, then we should expect to find that

$$\frac{\partial}{\partial T} (\log p_o/p_1) = 0$$

The value of $\log p_o/p_1$ for several concentrations

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1. Z. physik. Ch. 18, 572 (1895)

Table 4.

Conc	Δt_f	p_1	p_o	p_o-p_1 calc.	p_o-p_1 obs.	Diff.
0.05	0.175	17.509	17.539	0.030	0.029	0.001
0.1	0.345	17.480	"	0.059	0.057	0.002
0.2	0.679	17.414	"	0.115	0.113	0.002
0.3	1.007	17.368	"	0.171	0.168	0.003
0.4	1.333	17.312	"	0.227	0.222	0.005
0.5	1.665	17.256	"	0.283	0.278	0.005

Calculated Vapor Pressure Lowering of KCl Solutions at 20 from weighted mean Freezing Point Data of Noyes and Falk.

Table 5

Conc	Δt_f	p_o-p_1 calc.	p_o-p_1 obs.	Difference.
0.1121	0.384	0.065	0.064	0.001
0.2428	0.827	0.140	0.136	0.004
0.4136	1.389	0.236	0.232	0.004
0.6825	2.721	0.460	0.456	0.004
*1.0	3.286	0.555	0.554	0.001
1.0473	3.437	0.580	0.581	-0.001
1.4404	4.696	0.792	0.799	-0.007
1.9488	6.37	1.072	1.083	-0.011
2.2572	7.34	1.234	1.256	-0.022
2.6730	8.66	1.454	1.494	-0.040
3.3020	10.75	1.799	1.858	-0.059

*Raoult--The remainder of Raoult's work is included in the weighted means of Noyes and Falk.

Calculated Vapor Pressure Lowering of KCl Solutions at 20 from the Freezing Point Data of Roloff.

Table 6

Conc.	$\log p_o/p_1$ FP	$\log p_o/p_1$ 20°	Difference x 10^{-5}
0.05	.00074	.00072	2
0.1	00145	00142	3
0.1121	00162	00159	3
0.2	00286	00281	5
0.3	00425	00418	7
0.4136	00587	00578	9
0.8225	01154	01144	10
1.0473	01462	01463	-1
1.4404	02007	02025	-18
2.2572	03168	03228	-60
3.3020	04701	04863	-128

Values of $\log p_o/p_1$ as calculated from Freezing Point Data and from Vapor Pressure Data at 20.

Table 7

Conc.	$p_o - p_1$ KCl	$p_o - p_1$ Mannite	Percentage Ionization VP(20°)	CR(18°)	FP
0.05	0.0294	0.0156	88.5	88.9	88.5
0.07	0.0406	0.0215	86.2		
0.1	0.0574	0.0311	84.6	86.0	86.1
0.2	0.1128	0.0622	81.4	83.7	83.7
0.3	0.1680	0.0934	79.9		
0.4	0.2225	0.1243	79.0		
0.5	0.2785	0.1555	79.0	77.9	80.0
0.6	0.3347	0.1877	78.3		

Percentage Ionization of dilute solutions of Potassium Chloride Calculated from Vapor Pressure Lowerings and Compared with Values Calculated from Freezing Point and Conductance.

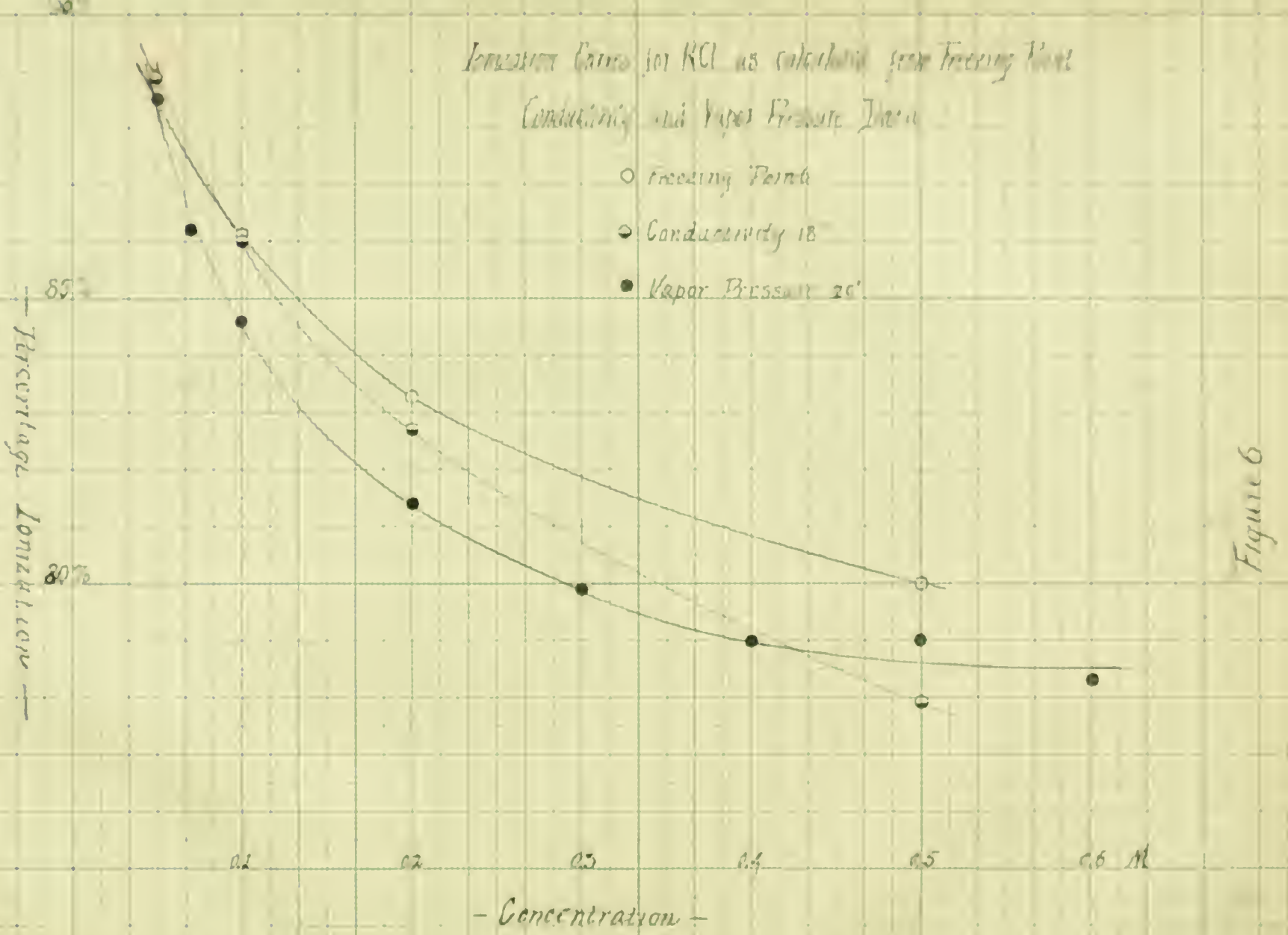

Figure 6

Figure 6

selected at random have been calculated at the freezing point and at 20 degrees. These values are recorded in Table 6. It is seen that the change in the value of log p_o/p_1 with temperature is not zero. In order for the value at the freezing point to be equal to that at 20 degrees for a solution as dilute as 0.3 M, we would have to assume an error of approximately 0.02 degrees in the freezing point lowering, or approximately 0.003 mm in the vapor pressure measurement. The peculiar change of

$$\frac{\partial}{\partial T}\left(\log \frac{p_o}{p_1} \right)$$

with concentration further supports the assumption that the departure from a linear function is caused by shifts of equilibrium between the water molecules.

3. Comparison of Ionization Values.

When the percentage ionization of dilute solutions of potassium chloride calculated from the vapor pressure lowerings recorded in this investigation is compared with those values obtained from the best freezing point and conductance ratio data a very good agreement is observed. See curves in figure 6. Table 7 contains the values compared with those compiled by Noyes and Falk.[1] The

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1. J. Am. Chem. Soc., 34, 489 (1912).

values under FP and CR are for concentrations expressed in mols per liter of solution, those under VP for solutions in mols per 1000 grams of solvent. The comparison does not involve any more serious error on account of the different modes of expressing concentration than might arise in the interpolation of the lowerings of the solutions.

Attention has already been called to the disturbing influences that produce irregularities in the lowering from 0.4 M upward. Any calculation of ionization for concentrations above that point could hardly be considered relaible.

It will be noticed that the ionization curves calculated from freezing point and from vapor pressure data are very similiar to each other and dissimiliar to the curve calculated from conductivity and viscosity data. This is to be expected, for in vapor pressure and freezing point observations, we are measuring properties of the solvent, while in conductance we are measuring properties of the solute. The lack of agreement of the values under FP and VP does not arise from the difference in temperature. Noyes and Falk in comparing the FP and CR values point out that the effect of temperature on ionization over such a short range of temperature is negligible. Then in this

difference between the VP and FP values we have a measure of the change of the complexity of water molecules between zero and 20 degrees.

SUMMARY.

The lowering of the vapor pressure of aqueous solutions of potassium chloride ranging from 0.05 M to 4.0 M has been studied by the improved static method of Frazer and Lovelace.

A more rapid and efficient method has been developed for making up air free solutions.

The relative accuracy of results previously obtained for potassium chloride solutions from 0.6 M to 2.0 M has been verified, in that $p_o - p_1/M$ is nearly constant.

The influence of the solvent is suggested as an explanation of some of the irregularities in lowering. Attention is called to the general way in which the molecular lowering curve follows the viscosity curve.

Through an equation connecting freezing point and vapor pressure, the vapor pressure of solutions has been calculated from freezing point data and compared to observed values.

The calculation of the percentage ionization of the dilute solutions studied shows good agreement with the values obtained from the best freezing point and conductivity data.

The measurement of the lowerings recorded herein is considered accurate to 0.001 mm.

BIOGRAPHY.

Virgil Bernard Sease was born in South Carolina September 13 1888. He received his early education in the public schools of Little Mountain, S. C. He was graduated from Newberry College, Newberry, S. C., in 1908 with the degree of Bachelor of Arts. During the next five years he was, first, principal in the Little Mountain High School, then, instructor in Newberry College. In the fall of 1913 he entered the Johns Hopkins University as a student in Chemistry. Physical Chemistry and Applied Electricity were his subordinate subjects. During the years 1914-15 and 1915-16 he was appointed Hopkins Scholar. He held a University Fellowship during the year 1916-17.